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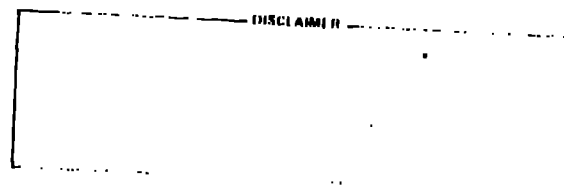
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MASTER

TITLE: USING DIFFUSION MEASUREMENTS TO DETERMINE PORE-SIZE DISTRIBUTIONS
IN POROUS MATERIALS.

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USING DIFFUSION MEASUREMENTS TO DETERMINE
PORE-SIZE DISTRIBUTIONS IN POROUS MATERIALS

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ABSTRACT

A method for determining pore-size distributions from diffusion measurements is presented. A Wicke-Kallenbach experiment, for measuring diffusion fluxes within porous materials, is carried out over a significant portion of the transition range between Knudsen flow and bulk diffusion. If the internal porous structure of the material is modeled as myriad nonintersecting cylindrical pores, an equation may be derived for the flux as a function of pressure, in which the flux is a functional of the pore-size distribution. The equation is a Fredholm integral equation of the first kind. This is an application of the general inversion problem, and solution of the equation for the pore-size distribution is possible. It is demonstrated from calculated fluxes using postulated ideal distributions that the method works very well for both unimodal and bimodal distributions. The method is not extraordinarily sensitive to experimental error. An example of a distribution obtained from a commercial porous catalyst is presented and compared with that obtained by mercury porosimetry.

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INTRODUCTION

The characteristics of a porous material's internal-void structure are important almost every time the material is involved in any sort of process. These processes range from the biological kind through catalysis, coal gasification, petroleum production, and others too numerous to mention.

Probably the first step in examining the internal pore structure of a material is the evaluation of its total internal-void volume by one of the capillary-filling methods described by Innes (1968) or by using the mercury and helium densities mentioned by Fass et al. (1974). Next would be the measurement of total surface area, both internal and external, using the elegantly practical physical adsorption method developed by Brunauer et al. (1938).

Beyond this, there is the recognition that the pores in a material do not all have the same size, and so a distribution of pore sizes must be determined. An unusually comprehensive review of methods for measuring pore-size distributions has been presented by Dullien and Batra (1970). Of the methods mentioned there, the nitrogen sorption-condensation and the mercury penetration methods have achieved popularity for measuring simple isotherms. Both of these techniques combine the virtues of reasonable and not overly-long experimental procedures with simple mathematical analyses. A jump upward in sophistication and realism in modeling pore-size distributions has come with the development, measurement, and use of a bivariate pore-size distribution by Dullien (1975).

Both the nitrogen sorption-condensation and the mercury penetration methods have significant drawbacks. Using them was a giant step forward in the ability to predict diffusion rates in porous catalysts, but the best techniques still can only forecast diffusion rates within a factor of two (Satterfield and Cadle, 1968; Brown et al., 1969). The forecasts for some predictable exceptions are even worse (Brown et al., 1969; Haynes and Brown, 1972). Scheidegger (1974) points out that permeability predictions based on mercury-penetration pore-size distributions have been very poor. These observations indicate that though the pore-size distributions from mercury penetration and nitrogen sorption-condensation do give valuable information concerning the internal-void structure, there is still much to measure which currently is not done

Using a bivariate distribution, Dullien (1975) was able to obtain quite good predictions of permeability in several sandstones. His bivariate distributions are obtained by combining mercury porosimetry with quantitative photomicrography. The latter technique is quite time-consuming, and thus one of the advantages of the simple methods is lost. It also has not yet been applied to pores with radii below about 1 μm. In addition, though it is well known that many porous materials are not isotropic, none of the methods discussed so far measure anisotropy in any fashion. New methods for determining pore-size distributions could well fill a need for giving more information about the internal-void structure of a porous material.

This paper presents a method for the determination of pore-size distributions from diffusion measurements. The method is an application of the general inversion problem that recently has been receiving attention in many fields (Allison, 1979). In this technique, the pore-size distribution must be obtained by the solution of a Fredholm integral equation of the first kind.

THEORY

The Fundamental Equation

An experiment for evaluating diffusion within porous materials was devised by Wicke and Kallenbach (1941) which measured steady-state counter-diffusion rates of two gases through one or more porous pellets. In this experiment, there are no temperature or pressure gradients across the pellet. This approach has been used widely, and detailed descriptions of modern apparatus and procedures for carrying out the Wicke-Kallenbach experiment are available both for pressures greater than atmospheric (Bell, 1971) and below atmospheric (Remick, 1972).

An equation has been developed which describes the dependence of a diffusion rate in the Wicke-Kallenbach experiment on the porosity of the solid, gases involved, pressure, temperature, and pore size. This equation, derived independently from different models by Evans et al. (1961) and by Scott and Dullier (1962), is

$$N_A = \frac{\varepsilon \, D_{AB} \, P}{R \, T \, L \, \tau} \ln \left[\frac{1 - \alpha y_{AL} + (D_{AB}/D_{KA})}{1 - \alpha y_{Ao} + (D_{AB}/D_{KA})} \right] \qquad (1)$$

in which

$$D_{AB} = (D_{AB}^{o})(P_{o}/P)(T/T_{o})^{1.75} \qquad (2)$$

For a cylindrical pore,

$$D_{KA} = (2/3)(8 \, RT/\pi M_A)^{1/2} \, (r) \qquad (3)$$

For a solid possessing cylindrical pores of a single radius, there are no adjustable parameters in Eq. (1). Given two gases, a temperature, and a pressure, one can determine the diffusion rates of the gases through a solid pierced by parallel pores of a single radius. The validity of this equation for bundles of single-radius capillaries at room temperature over a wide range of pressure was confirmed experimentally by Remick and Geankoplis (1973).

There are limiting forms of Eq. (1) at both high and low pressures. At high pressures, the equation can be simplified to

$$N_A = \frac{\epsilon\, D_{AB}\, P}{R\,T\,L\,\alpha} \ln \left[\frac{1 - \alpha\, y_{AL}}{1 - \alpha\, y_{Ao}} \right] \tag{4}$$

and at low pressures, Eq. (1) becomes

$$N_A = \frac{\epsilon\, D_{KA}\, P}{R\,T\,L} (y_{Ao} - y_{AL}) \tag{5}$$

To use Eq. (1) in the derivation of an equation to describe the total flux through a real porous solid with pores of varying size, shape, and inter-connectivity, a model of the porous substance must first be postulated. The most common model of a porous material's internal-void structure is myriad randomly oriented nonintersecting cylindrical pores piercing the solid. The various pores may have different radii.

Using this model, an equation may be developed for the total diffusive flux through a porous solid in the Wicke-Kallenbach experiment. A pore-size distribution function $f(r)$ is defined so that $f(r)dr$ is the fraction of the total pore volume that is composed of pores with radii between r and $r + dr$. If all the pores are oriented in the direction of diffusive flow, then it follows from Eq. (1) that the total flux through the porous solid is

$$N_A = \frac{\epsilon\, D_{AB}\, P}{R\,T\,L\,\alpha} \int_{r_{min}}^{r_{max}} \left\{ \ln \left[\frac{1 - \alpha y_{AL} + (D_{AB}/D_{KA})}{1 - \alpha y_{Ao} + (D_{AB}/D_{KA})} \right] \right\} f(r)dr \tag{6}$$

If the pores are not all oriented in the direction of diffusive flow, but rather are oriented randomly, then the total flux given by Eq. (6) is divided by a tortuosity factor. For randomly oriented, nonintersecting pores, the tortuosity factor equals three (Feng and Stewart, 1973). Thus the equation for the total diffusive flux through our model porous material is

$$N_A = \frac{\epsilon\, D_{AB}\, P}{3R\,T\,L\,\alpha} \int_{r_{min}}^{r_{max}} \left\{ \ln \left[\frac{1 - \alpha y_{AL} + (D_{AB}/D_{KA})}{1 - \alpha y_{Ao} + (D_{AB}/D_{KA})} \right] \right\} f(r)dr \tag{7}$$

If Eqs. (2) and (3) are substituted into Eq. (7), and if a Wicke-Kallenbach experiment is carried out at a single temperature over a range of pressures, the resulting equation is

$$N_A = \left[\frac{\varepsilon\, D^o_{AB} P_o (T/T_o)^{1.75}}{3R\, T\, L\, \alpha}\right]$$

$$\int_{r_{min}}^{r_{max}} \left\{ \ln\left[\frac{1 - \alpha y_{AL} + \{(3D^o_{AB}P_o T^{1.75})/[(2rPT_o^{1.75})(8RT/\pi M_A)^{1/2}]\}}{1 - \alpha y_{Ao} + \{(3D^o_{AB}P_o T^{1.75})/[(2rPT_o^{1.75})(8RT/\pi M_A)^{1/2}]\}}\right]\right\} f(r)dr \quad (8)$$

The functional dependence of this equation can be represented as

$$N_A(P) = \lambda \int_a^b K(P,r) f(r) dr \quad (9)$$

This is a Fredholm integral equation of the first kind. If the kernel $K(P,r)$ is a known function and the function $N_A(P)$ is also known while $f(r)$ is not, under some conditions the function $f(r)$ may be obtained. Since $f(r)$ is the pore-size distribution we are seeking, solution of the equation will yield the desired goal.

The equation cannot be solved to yield the distribution $f(r)$ at either high or low pressures. At high pressures, where bulk diffusion completely limits the flow rate, Eq. (8) becomes

$$N_A = \frac{\varepsilon D^o_{AB} P_o (T/T_o)^{1.75}}{3R\, T\, L\, \alpha} \left[\ln \frac{1 - \alpha y_{AL}}{1 - \alpha y_{Ao}}\right]\int_{r_{min}}^{r_{max}} f(r)dr \quad (10)$$

In this case, N_A is not a function of P, so no unique solution of the equation for the function $f(r)$ is possible.

At low pressures, where Knudsen flow limits the flux, Eq. (8) becomes

$$N_A = \frac{2 \, \varepsilon \, P \, (y_{Ao} - y_{AL})}{3(\pi \, RTM_A)^{1/2} L} \int_{r_{min}}^{r_{max}} r \, f(r) dr \qquad (11)$$

When this equation is valid. N_A is a function of P, but the value of the integral does not change when P changes. Therefore no unique solution of the equation for $f(r)$ is possible.

However, for the transition region between the bulk diffusion and Knudsen flow regimes, it is possible to solve Eq. (8) for $f(r)$, and so the pore-size distribution may be obtained from a Wicke-Kallenbach experiment carried out over the proper pressure range. The method for obtaining the distribution from the flux data is discussed in the next section.

Solution of the Equation

A Fredholm integral equation of the first kind has the form (Irving and Mullineaux, 1959):

$$\eta(x) = \int_a^b K(x,t) \, \phi(t) \, dt \qquad (12)$$

in which $\phi(t)$ is unknown. If $K(x,t)$ and $\phi(t)$ are reasonably smooth functions of t, the integral Eq. (12) can be approximated very closely by the finite difference analog

$$\eta(x_i) = \sum_{j=1}^{M} K(x_i, t_j) \, \phi(t_j) \, \delta t_j \quad , \quad i = 1, \, 2, \, \ldots, \, N, \qquad (13)$$

for suitably chosen x_i in the interval $[c,d]$ and t_j in the interval $[a,b]$. In matrix notation, (13) becomes

$$\underline{n} = (\underline{\underline{K}} \ \underline{\underline{\delta t}})_{\Phi} \tag{14}$$

where $\underline{\underline{\delta t}}$ is a diagonal matrix whose diagonal elements are the weighting factors for the integration interval. The straightforward approach to solving this, namely, writing

$$\underline{\Phi} = \underline{\underline{\delta t}}^{-1} \ \underline{\underline{K}}^{-1} \ \underline{n}, \tag{15}$$

does not work in most inverse problems. Wildly oscillating "solutions" are obtained as M is increased. An example of this catastrophic behavior is shown in Allison's paper (1979). The same difficulty occurs in the present situation when Eq. (15) is applied to Eq. (8).

The reason for the instability of this simple inversion approach lies in the smoothness of the kernel and the accuracy with which the data function, n, is known. In Eq. (12), $\phi(t)$ can be replaced by $\phi + \psi_n$ where ψ_n represents a high frequency function (such as $\sin nt$). If K is a smooth continuous function, then the contribution of ψ_n for sufficiently large n will be equal to or less than the error present in $n(x)$. In other words, the smooth kernel does not allow high frequency components to be discriminated against. Consequently, on inversion, there is no way to determine the relative contributions of high frequency components.

An acceptable approach to this problem is known and is commonly called the method of regularization (Tihonov, 1963). The Fredholm equation of the first kind (12) is replaced with

$$\int_a^b \overline{K}(s,t)\phi_1(t)dt + \beta H \ [\psi_1(s)] = \overline{n}(s) \tag{16}$$

where $H[\psi_1]$ is a differential operator (usually equal to $\phi_1(s) + k\phi_1'(s)$

where k is an arbitrary positive function), $\overline{K}(s,t) = \int_{c}^{d} K(\xi,s)K(\xi,t)d\xi$ and

$\overline{\eta}(s) = \int_{-c}^{d} K(x,s)\overline{\eta}(x)dx$; this is a general integral equation of the second kind.

These equations are generally well behaved. As β approaches zero, ϕ_1 in Eq. (16) approaches ϕ in Eq. (13). When the integrals in Eq. (16) are approximated by summations of finite increments and the result written in matrix form, one obtains

$$\left[\underline{\underline{K}}^{*} \ \underline{\underline{\delta x}} \ \underline{\underline{K}} \ \underline{\underline{\delta t}} + \beta \ \underline{\underline{H}} \right] \underline{\phi_1} = \underline{\underline{K}}^{*} \ \underline{\underline{\delta x}} \ \underline{\eta} \tag{17}$$

where $\underline{\underline{K}}^{*}$ is the transpose of $\underline{\underline{K}}$, $\underline{\underline{\delta x}}$ is a diagonal matrix whose elements are the weighting factors for the interval [c,d].

There is a value of ϕ which provides the best approximation $\phi_1(t)$ to $\phi(t)$. In practice, Eq. (17) is solved repeatedly for $\phi_1(t)$, using steadily decreasing values of β. If β is allowed to become too small (generally, less than the error level in η), the solution becomes unstable. The closest approach of ϕ_1 to ϕ is determined by searching for the value of β which minimizes the functional

$$J = \sum_{i=1}^{N} \left[\eta(x_i) - \sum_{j=1}^{M} K(x_i,t_j)\phi_1(t_j)\Delta t_j \right]^2 \tag{18}$$

An additional constraint which improves the determination of $\phi_1(t)$ is the requirement that $\phi_1(t) \geq 0$. Negative values of pore-size distributions are meaningless.

This is the method used to determine the pore-size distributions presented in the following sections of this paper. Further details of this technique, its history, fundamentals, and generalizations of it, can be found in the paper by Allison (1979).

TESTS OF THE METHOD

The first tests evaluated the method under ideal conditions. Two porous solids containing particular pore-size distributions were pictured and fluxes calculated that would be obtained experimentally with such materials. Using the calculated fluxes, pore-size distributions were determined by the proposed method and compared with the original postulated distributions. In other words, a distribution $f(r)$ was stipulated, and N_A as a function of P was determined employing Eq. `) with N_A as the unknown. Using the calculated $N_A(P)$, the situation was then reversed, and Eq. (8) with $f(r)$ as the unknown was used to determine $f(r)$ by the numerical technique described in the preceding section.

The first theoretical distribution was a normal one centered about a pore radius of 50 nm:

$$f_1(r) = 0.03989 \exp\left[-\frac{1}{200}(r - 30)^2\right] \tag{19}$$

with r in nanometers. The second theoretical distribution was bimodal, with components distributed normally around pore radii of 5 and 50 nm. One-half of the total pore volume was in each segment f the distribution. The distribution was:

$$f_2(r) = 0.1995 \exp\left[-\frac{1}{2}(r - 5)^2\right] + 0.01995 \exp\left[-\frac{1}{200}(r - 50)^2\right] \tag{20}$$

Again, r in this distribution is in nanometers.

The conditions used for the calculations were:

c	0.5
Temperature, K	298
y_{Ao}	1.0
y_{AL}	0.0
Test 1 Pressure Range, MPa	0.1 - 2.0
Test 2 Pressure Range, MPa	0.1 - 2.0
	0.1 - 30.0

In the first test, fluxes were calculated using the postulated simple normal distribution and a 20-fold pressure range typical of experimental studies (Haynes, 1969). Figure 1 presents the results of this test. The curve is the postulated normal distribution, and the circles are the values of the distribution determined using the proposed method. Twenty-one points from the calculated-flux curve were employed. The agreement between the postulated curve and the one determined by the proposed method is excellent, with only a slight difference between the postulated curve and the determined one at the center of the distribution.

The first test showed that the performance of the method is very good when the distribution is a simple one. Using a bimodal distribution gives a much more severe trial, however, and the second test did this. Following the same procedure as in the first test, a pore-size distribution was determined using the proposed method and compared with the postulated bimodal distribution. The results are shown in Fig. 2. The solid curve is the postulated distribution, the triangles were obtained using the 20-fold pressure range of the first test, and the circles came from using a 300-fold pressure range. Even from the lower pressure range, the two peaks are easily discernible, while they are quite well defined using the higher pressure range.

A third test of the method checked its sensitivity to small experimental errors. Haynes (1969) obtained diffusion data from Wicke-Kallenbach experiments using several different porous catalysts and adsorbents. Using his data for Girdler catalyst G-3B, a smooth curve of N_A as a function of P was drawn, and points from this were used to obtain a pore-size distribution. Also, straight lines were drawn between Haynes' data points, and another distribution was obtained. The two were compared; the difference between the two curves was slight. The maximum difference between the two curves was less than two percent and over most of the range was less than one percent.

It is of interest to compare the pore-size distribution for the Girdler G-3B obtained from Haynes' diffusion data with that which Haynes obtained by mercury porosimetry. This is done in Fig. 3. The differences are significant. The diffusion-pore-size distribution is much broader, has the shape of an approximately Maxwellian distribution, and has a maximum at about 1L.5 nm. The porosimetry-pore-size distribution has the shape of a roughly normal distribution, is very narrow, and has a peak at about 30 nm. Differences such as these are being investigated currently.

CONCLUSION

A method of obtaining pore-size distributions from diffusion measurements has been presented. Work on this method is continuing, especially in the areas of improving the technique of solving the Fredholm integral equation to obtain the distribution, and in the comparison of pore-size distributions determined by this method and those obtained by other techniques.

NOTATION

a   lower limit on a definite integral

b   upper limit on a definite integral

D   diffusivity, cm^2/s

f(r)   pore-size distribution function, in which $f(r)dr$ is the fraction of pore volume with pore radii between r and $r + dr$, cm^{-1}

K   function of two variables; the kernel in the Fredholm integral equation, dimensionless

L   length of diffusion path, cm

M   molecular weight, g/gmole

N   diffusion flux, $gmole/(cm^2)(s)$

P   pressure, Pa

R   gas constant, $(cm^3)(Pa)/(gmole)(K)$

r   pore radius, cm

t   variable in Fredholm integral equation

T   temperature, °K

x   variable in Fredholm integral equation

y   mole fraction of diffusing gas

Greek letters

α   parameter related to ratio of molecular weights

β   smoothing parameter in modified Fredholm integral equation

ε   porosity of porous material

η   function of x

λ   parameter in Fredholm integral equation

φ   function of t

Subscripts

A   of substance A

AB   of substance A in the presence of B

AL   of substance A at the distant face of the porous material

Ao   of substance A at the near face of the porous material

KA   of substance A in the Knudsen-flow regime

max   maximum value present in the porous material

min   minimum value present in the porous material

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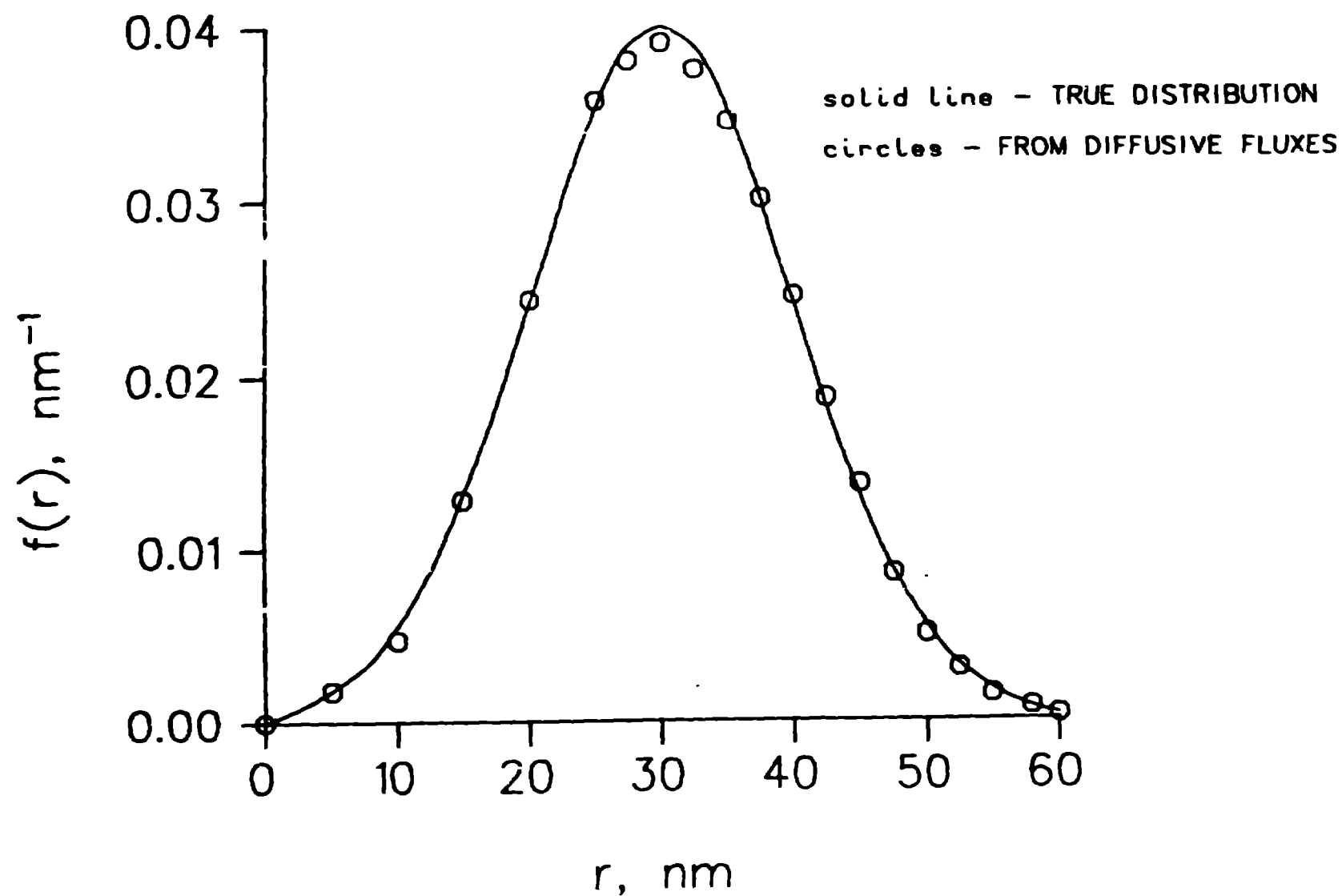
FIG. 1 PORE-SIZE DISTRIBUTION DETERMINED FROM DIFFUSIVE FLUXES --
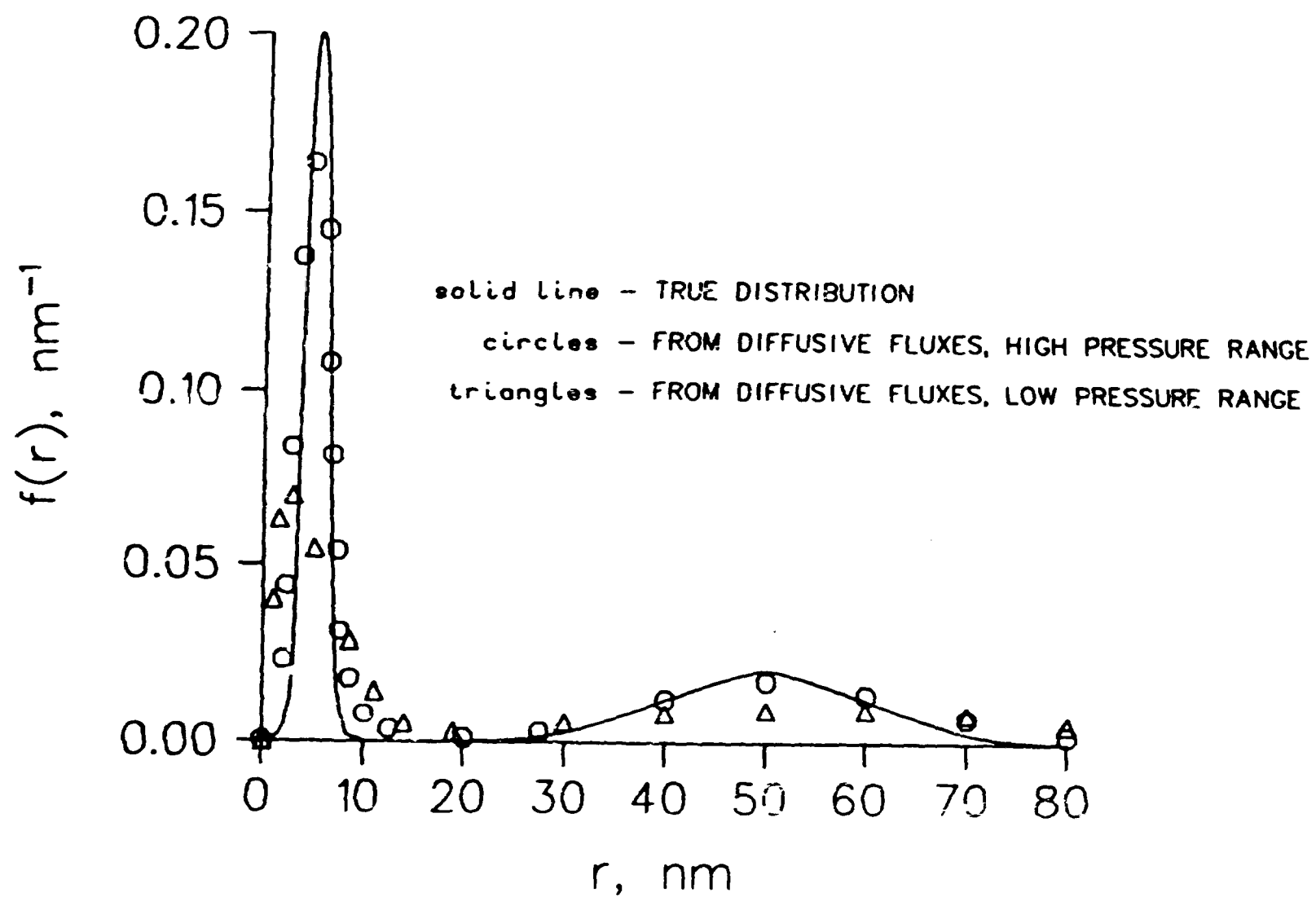SIMPLE NORMAL DISTRIBUTION OF PORE SIZES

FIG. 2 PORE–SIZE DISTRIBUTION DETERMINED FROM DIFFUSIVE FLUXES ––
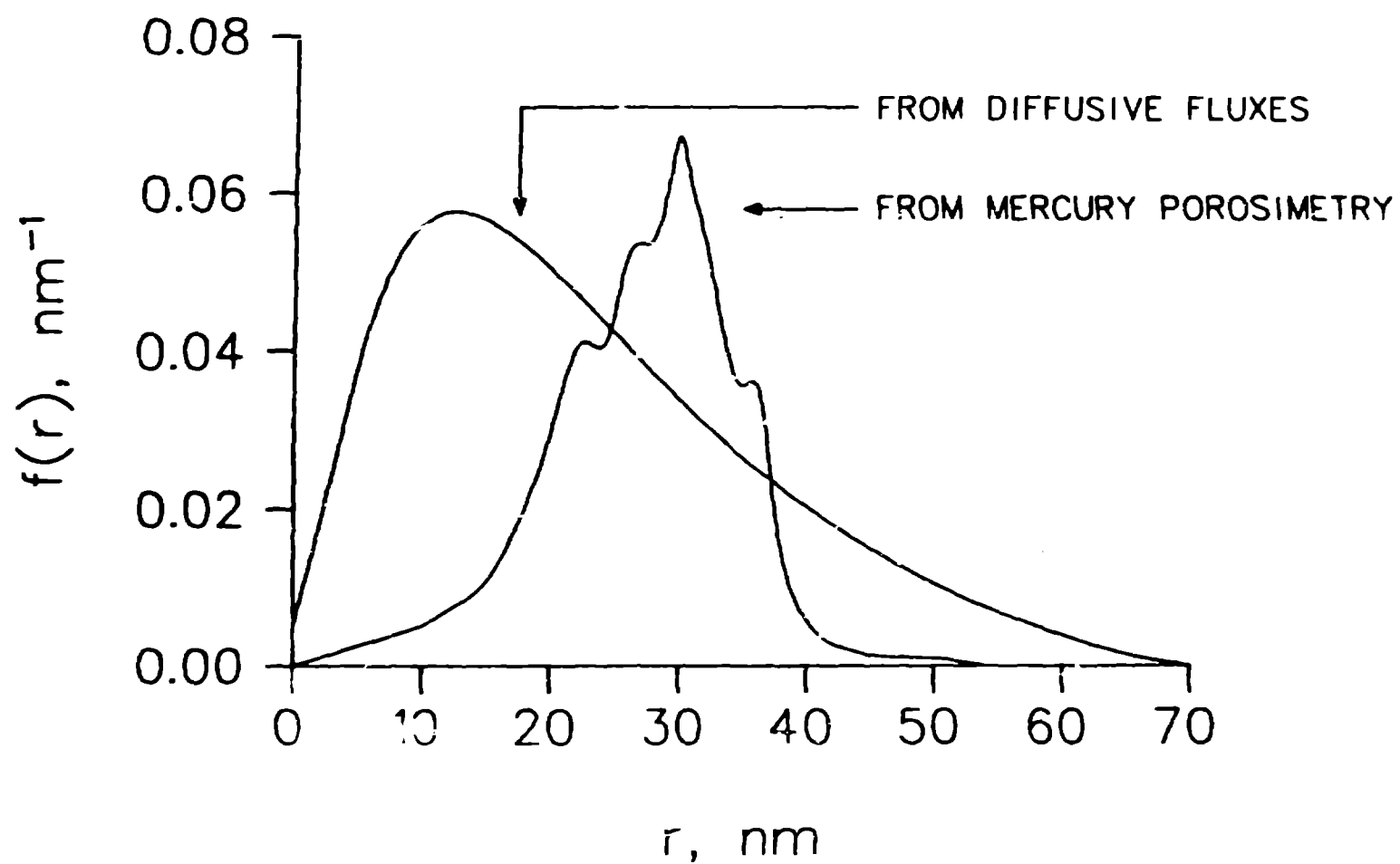BIMODAL DISTRIBUTION OF PORE SIZES

FIG. 3   COMPARISON OF PORE-SIZE DISTRIBUTIONS DETERMINED FROM DIFFUSIVE FLUXES AND FROM MERCURY POROSIMETRY